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(56) Documents Cited

GB 1325847 A GB 1304238 A  
GB 0886885 A GB 0717050 A  
DE 019726620 A  
WPI Abstract Accession No 1991-365153 &  
JP030244690A

(58) Field of Search

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(54) Abstract Title

**Preparation of polymer-modified bitumen compositions**

(57) A process for the preparation of a polymer-modified bitumen, comprises preparing a mixture of a bitumen and a cross-linkable polymer, blowing the mixture with an oxygen-containing gas preferably air at a temperature in the range of from 100 to 240°C, and adding sulphur to the mixture whilst it is being blown. The polymer component is preferably a linear styrene-butadiene-styrene block copolymer. The composition is useful in paving applications.

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A Process for the Preparation of Polymer-Modified  
Bitumen Compositions

The present invention relates to a process for the preparation of a polymer-modified bitumen composition, and a polymer-modified bitumen composition obtainable by said process.

5 Background of the Invention

Bitumen is a very widely used civil engineering material being regularly employed in the construction of roads etc. and in industrial applications, for example as a roofing material, a pipe coating or an adhesive.

10 Whilst bitumen is in many respects naturally suitable for use in such applications, it is often inherently deficient in some physical properties it would be desirable to improve. For example, whilst bitumen generally performs well as a binder in asphalt mixes for  
15 paving applications e.g. for roads, runways or parking spaces, increasingly heavy traffic loads have led to the premature wear of paving surfaces through cracking and rutting. Accordingly, bitumen has been continually developed to meet ever-increasing performance demands.

20 One way in which the properties of bitumen may be modified is by the addition of polymers and efforts have been made to improve the properties of bitumen by addition of polymers such as neoprene, ethylene vinyl acetate copolymers (EVA), polyolefins, conjugated diene  
25 rubbers and styrenic block copolymers such as styrene-butadiene-styrene and styrene-isoprene-styrene block copolymers.

However, whilst such polymer-modified bitumen has in many instances been shown to give improved performance in

a wide range of bitumen applications, use has been restricted as many mixtures of bitumen and polymer are non-homogeneous. Polymer-bitumen blends are two phase systems; bitumen itself being a complex mixture of molecular structures which include maltenes and asphaltenes. The addition of a polymer to bitumen disturbs this equilibrium and leads to phase separation particularly on hot storage into a polymer-rich layer and an asphaltene-rich layer, each of which have distinctly different properties.

Such phase separation can be avoided or reduced by the use of polymer compatible bitumen having low asphaltene content and high aromaticity. However, there is a limited availability of such compatible bitumen, in particular of the harder grades of bitumen suitable for use in paving applications. Therefore, there is a need for a means by which otherwise incompatible polymer-bitumen blends can be made homogeneous or storage stable.

Attempts have been made to achieve this by adding sulphur-containing compounds to polymer-bitumen blends as coupling agents, wherein a compound is added which acts a sulphur-donor or an agent to yield free sulphur during the polymer-modified bitumen preparation process. Examples of such agents include dialkyl sulphides, diarylsulfides, vulcanization agents (morpholino disulphide and polyalkyl phenol sulphides) and vulcanization accelerators (tetramethyl thiuram disulphide). In each case it is necessary that free sulphur be generated in the blending process to give rise to improved homogeneity or storage stability.

Sulphur-donor agents are used as the addition of elemental sulphur to hot bitumen produces significant quantities of hydrogen sulphide gas. This is problematic as bitumen-polymer blends are generally prepared at

mixing plants lacking the facilities to contain the release of such a gas. Therefore, it would be advantageous if sulphur could be added to a bitumen at a bitumen-polymer mixing site in a manner which minimised the release of hydrogen sulphide gas.

#### Summary of the invention

A new and efficient process for converting incompatible polymer-bitumen blends into homogeneous blends has now been established, which comprises the direct addition of sulphur to a mixture of bitumen and cross-linkable polymer whilst said mixture is being blown, and which results in the emission of little or no hydrogen sulphide gas.

Accordingly, the present invention provides a process for the preparation of a polymer-modified bitumen composition, which process comprises preparing a mixture of a bitumen and a cross-linkable polymer, blowing the mixture with an oxygen-containing gas at a temperature in the range of from 100 to 240 °C, and adding sulphur to the mixture whilst it is being blown.

#### Detailed description of the invention

The mixture of bitumen and cross-linkable polymer to be blown in the process of the present invention may be prepared using standard techniques known in the art, for example by mixing the polymer into the bitumen at elevated temperature. In such a process the mixing may be conveniently performed in a high shear mixer, and the temperature of the bitumen may be conveniently in the range of from 160 to 220 °C.

The bitumen used to prepare the mixture may be a residue from the distillation of crude oil, a cracked residue, a naturally occurring bitumen or a blend of various bitumen types.

Examples of bitumen that may be conveniently used to prepare the mixture include distillation or "straight run" bitumen, and precipitation bitumen, e.g. propane bitumen. Other bitumen that may be used include mixtures of one or more of these bitumen with extenders such as petroleum extracts, distillates or residues, and oils. Preferably the bitumen is a distillation or "straight run" bitumen, optionally containing an extender.

It is an advantageous feature of the present invention that stable polymer-bitumen blends may be prepared from harder grades of bitumen. Accordingly, the bitumen to be used in the mixture preferably has a penetration of from 5 to 100 dmm (measured according to EN 1426), more preferably of from 10 to 90 dmm and most preferably of from 25 to 55 dmm. The softening point of the bitumen is preferably in the range of from 40 to 130 °C (measured according to EN 1427), more preferably of from 45 to 80 °C.

The cross-linkable polymer of the mixture may be any polymer which when contacted with sulphur forms sulphur cross-links between polymer chains, i.e. polymers containing unsaturated units. Examples of polymers that may be used include polyisoprene, polybutadiene, polyacrylate, polymethacrylate and random or block copolymers of a conjugated diene, (e.g. butadiene, isoprene, pentadiene, hexadiene or chloroprene) and a monovinyl aromatic hydrocarbon (e.g. styrene, methylstyrene, vinylnaphthalene, vinyltoluene or vinylxylene).

In a preferred embodiment of the present invention, the cross-linkable polymer of the mixture is a thermoplastic rubber. Whilst a wide range of thermoplastic rubbers may be used, the thermoplastic rubber is preferably a block copolymer comprising at

least two terminal poly(monovinyl aromatic hydrocarbon) blocks and at least one central poly(conjugated diene) block, forming a continuous network.

Preferably the block copolymer is selected from the group consisting of those of formulae  $A(BA)_m$  or  $(AB)_nX$ , wherein A represents a block of predominantly poly(monovinylaromatic hydrocarbon), wherein B represents a block of predominantly poly(conjugated diene), wherein X represents the residue of a multivalent coupling agent and wherein n represents an integer  $\geq 1$ , preferably  $\geq 2$ , and m represents an integer  $\geq 1$ , preferably m is 1.

More preferably the A blocks represent predominantly poly(styrene) blocks and the B blocks represent predominantly poly(butadiene) or poly(isoprene). Most preferably the B blocks are predominantly poly(butadiene). Multivalent coupling agents to be used include those commonly known in the art.

With the term "predominantly" it is meant that the respective blocks A and B may be mainly derived from monovinyl aromatic hydrocarbon monomer and conjugated diene monomer, which monomers may be mixed with other structurally related or non-related co-monomers, e.g. mono-vinyl aromatic hydrocarbon monomer as main component and small amounts (up to 10%) of other monomers or butadiene mixed with isoprene or with small amounts of styrene. More preferably the copolymers contain pure poly(styrene), pure poly(isoprene) or pure poly(butadiene) blocks.

Preferably the A blocks of the block copolymers have an apparent mol wt. in the range of from 3,000 to 100,000, preferably in the range of from 5,000 to 40,000; whilst the B blocks preferably have an apparent mol wt. in the range of from 10,000 to 250,000 and preferably in

the range of from 40,000 to 200,000. The originally prepared poly(conjugated diene) blocks usually contain in the range of from 5 to 50 mol% vinyl groups, originating from 1,2 polymerisation relative to the conjugated diene molecules, and preferably a vinyl content in the range of  
5 from 10 to 25%.

The block copolymers to be used according to the present invention, preferably contain polymerised vinyl aromatic monomers in an amount in the range of from 10 to  
10 60% by weight, more preferably in the range of from 15 to 45% by weight.

The apparent molecular weight of the total block copolymer will preferably be in the range of from 15,000 to 350,000 and more preferably in the range of from  
15 40,000 to 250,000.

Preferred cross-linkable polymers for use in the present invention are available from Kraton B.V. (Kraton is a trade mark).

The amount of cross-linkable polymer in the mixture of bitumen and cross-linkable polymer is preferably at  
20 least 3% wt, more preferably at least 4% wt, even more preferably at least 5% wt, and most preferably in the range of from 3% wt to 20% wt, preferably 5% wt to 10% wt, based on total amount of bitumen and cross-linkable  
25 polymer.

The amount of bitumen in the mixture of bitumen and cross-linkable polymer is preferably no more than 97 %wt, more preferably no more than 96% wt, even more preferably no more than 95% wt, and most preferably in the range of  
30 from 80 to 97% wt, preferably 90 to 95% wt, based on total amount of bitumen and cross-linkable polymer.

The process of the present invention is particularly useful when preparing polymer-modified bitumen comprising larger amounts of polymer, e.g. at least 3% wt or

greater, as the larger the amount of polymer the more susceptible the polymer-bitumen blend will be to phase separation.

5 In the process of the present invention, sulphur is added to the mixture of bitumen and cross-linkable polymer whilst said mixture is subjected to blowing. Blowing is a conventional process well known to those skilled in the art, wherein the properties of a bitumen are modified by blowing a gas through the bitumen at high temperature (see  
10 Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Volume 3, p 299-304). There are two general types of blown bitumen: fully blown bitumen, wherein the bitumen is blown under vigorous conditions at high blowing temperatures; and semi-blown bitumen or air-rectified  
15 bitumen, wherein less modification of bitumen properties is required and bitumen is blown under milder conditions.

In the present invention the blowing conditions need not be severe, and it is a feature of the present invention that it comprises blowing the mixture at a  
20 temperature in the range of from 100 to 240 °C, preferably of from 120 to 200 °C, and most preferably of from 150 to 180 °C.

The gas used to blow the mixture of bitumen and cross-linkable polymer is an oxygen-containing gas, for  
25 example oxygen or air. Most preferably the mixture is blown with air.

In the present invention, the rate at which the gas is blown into the mixture of bitumen and cross-linkable polymer need not be high and the injection rate of the gas  
30 into the mixture is conveniently kept as low as possible whilst maintaining efficient mixing of the mixture. Preferably, the gas injection rate of the oxygen-containing gas is less than 10,000 l/h, more preferably less than 8,000 l/h, and most preferably less than 7,500



1/h. The gas injection rate is preferably at least 2,000  
1/h.

During blowing, sulphur may be conveniently added to  
the mixture of bitumen and cross-linkable polymer in a  
5 single portion or in several portions. Preferably the  
sulphur is added in several portions over a period of less  
than 2 hours, more preferably less than 1 hour. The  
amount of sulphur added may vary depending on the type of  
bitumen and cross-linkable polymer in the mixture, however  
10 the amount of sulphur added will preferably be in the  
range of from 0.01 to 2 % wt, more preferably in the range  
of from 0.01 to 1% wt, even more preferably in the range  
of from 0.02 to 0.5 % wt, and most preferably in the range  
of from 0.05 to 0.2 % wt, based on the total amount of  
15 bitumen and cross-linkable polymer in the mixture.

The sulphur is preferably elemental sulphur. The  
purity of the sulphur is not critical. However, in order  
to limit the risk of product contamination the sulphur is  
preferably at least 95.0% pure, more preferably at least  
20 99.0% pure, even more preferably at least 99.5% pure, and  
most preferably at least 99.9% pure.

Following the addition of the sulphur the mixture is  
preferably blown for a period of time of less than 6  
hours, more preferably of less than 3 hours and most  
25 preferably in the range of from 0.5 to 3 hours.

It is an advantageous feature of the present  
invention that little or no hydrogen sulphide gas is  
emitted during the process. It is thought that by blowing  
the mixture of bitumen and cross-linkable polymer during  
30 sulphur addition, the hydrogen sulphide gas generated in  
the process is substantially converted to other less  
noxious gasses, thus removing the need for containment  
apparatus to collect off-gasses. Further, as only mild  
blowing conditions need be employed in the process the

properties of the polymer-bitumen blend are not significantly altered, as they would be if the mixture was fully-blown, e.g. at a temperature in excess of 240 °C.

5 The present invention further provides a polymer-modified bitumen composition obtainable by the process of the present invention. The polymer-modified bitumen composition preferably has a penetration of from 5 to 100 dmm (measured according to EN 1426), more preferably of from 10 to 90 dmm and most preferably of from 25 to 55  
10 dmm. The softening point of the bitumen is preferably in the range of from 40 to 130 °C (measured according to EN 1427), more preferably 60 to 90 °C.

Fillers such as carbon black, silica and calcium carbonate, stabilisers, antioxidants, pigments, and  
15 solvents known to be useful in bitumen compositions can be incorporated into the polymer-modified compositions of the present invention.

The polymer-modified bitumen compositions prepared by the process of the present invention may be used in a  
20 variety of applications, for example as pipe coatings, roofing materials or in paving applications (i.e. in asphalt mixtures of bitumen and aggregate to be used in the construction of roads, runways or parking spaces etc.) The process of the present invention may very  
25 conveniently be used to prepare polymer-modified compositions for use in paving applications, in particular in asphalt mixtures for road applications. Accordingly, in a preferred embodiment the present invention provides a process of preparing a paving-grade  
30 polymer-modified bitumen composition.

The present invention still further provides for the use of a polymer-modified bitumen composition according to the invention in paving applications, preferably in an asphalt mixture for road applications.

The invention will be further understood from the following illustrative examples.

Two conventional polymer-bitumen blends were prepared by mixing a linear styrene-butadiene-styrene  
5 block copolymer having an apparent molecular weight of 150,000 g/mol, and a polystyrene content of 30 % wt (Kraton D 1192; obtained from Kraton B.V.) with a base bitumen in a high shear mixer at a temperature of approximately 180 °C. The contents of the conventional  
10 polymer-bitumen blends (A) and (B) are detailed below. The base bitumen employed were straight run bitumen, the base bitumen of mixture (B) additionally comprising approximately 14 % wt of a petroleum extract extender.

Mixture (A): Bitumen (penetration 40 dmm; softening  
15 point 52 °C), 95 % wt; Kraton D 1192, 5 %wt.

Mixture (B): Bitumen (penetration 90 dmm; softening  
point 45 °C), 93 % wt; Kraton D 1192, 7 %wt.

20 Samples of conventional polymer-bitumen blends (A) and (B) were taken for analysis; their properties being shown in Table 1.

Subsequently, conventional polymer-bitumen blends (A) and (B) were each treated with sulphur as follows. The  
25 mixtures of bitumen and polymer were transferred to a blowing unit wherein they were maintained at an elevated temperature and blown with air. The blowing conditions used were mild, each mixture being maintained at a temperature of approximately 170 °C and the air injection  
30 rate being kept below 7,500 l/h, i.e. as low as possible whilst maintaining efficient mixing of the batch.

Whilst the mixture was being blown, 0.1 % wt of sulphur, based on total amount of bitumen and polymer in

the mixture, was added to the mixture in several portions. During the process the concentration of sulphur dioxide in the off-gases was measured using infrared spectroscopy. After sulphur addition, sulphur dioxide concentration rose rapidly and then dropped back to its original level over a period of approximately 30 minutes. No hydrogen sulphide was detected during the process. The sulphur employed was granulated elemental sulphur (Sulphur content min. 99,9%) obtained from the Metallgesellschaft GmbH, Frankfurt, Germany. On completion, the sulphur-treated polymer-modified bitumen compositions (A') and (B') were allowed to cool and samples taken for analysis.

The storage stability of the polymer-modified bitumen compositions was measured both before and after sulphur treatment using test TL-PMB chapter 3.3.3 (issued 1991). In this method, a 20 cm high sample of polymer-modified bitumen composition is heated in an oven at 180 °C for 72 hours. The sample is then removed from the oven and cut into three vertical segments, and the softening point of the top and bottom segments measured. If the composition has good homogeneity the softening point of the top and bottom segments will be similar; the specification of a homogenous composition being a difference in softening point of 2 °C or less. Differences in softening point greater than 2 °C denote non-homogeneous compositions.

The properties of polymer-modified bitumen compositions before [(A) and (B)] and after [(A') and (B')] sulphur treatment are shown in Table 1. The storage stability values denote the difference in softening point between the top and bottom segments according to TL-PMB chapter 3.3.3 (issued 1991).

Table 1

Polymer-Modified Bitumen Composition	(A)	(A') (0.1% wt sulphur)	(B)	(B') (0.1% wt sulphur)
Blowing Time (min)	-	180	-	100
Temperature (°C)	-	170	-	170
Storage Stability (Δ°C)	35.5	0.5	>20.0	1.0
Softening Point (°C)	74.5	86.0	90.0	85.5
Penetration (dmm)	33	31	49	50
Fraass Break Point (°C)	-10.0	-17.0	-34.0	-22.0

Test Methods Used:

- Penetration at 25°C (EN 1426)
- 5 - Softening point (EN 1427)
- Fraass Breakpoint (EN 12593)
- Storage stability (TL-PMB chapter 3.3.3; issued 1991)

10 From Table 1 it can be seen that without sulphur treatment polymer-modified bitumen compositions (A) and (B) are non-homogeneous, whilst after treatment with sulphur according to the present invention, during which no release of hydrogen sulphide was detected, the compositions (A') and (B') display excellent homogeneity.

C L A I M S

1. A process for the preparation of a polymer-modified bitumen composition, which process comprises preparing a mixture of a bitumen and a cross-linkable polymer, blowing the mixture with an oxygen-containing gas at a temperature in the range of from 100 to 240 °C, and adding sulphur to the mixture whilst it is being blown.
2. A process as claimed in claim 1, wherein the mixture is blown with an oxygen-containing gas at a temperature in the range of from 150 to 180 °C.
3. A process as claimed in claim 1 or claim 2, wherein the gas injection rate of the oxygen-containing gas is less than 10,000 l/h.
4. A process as claimed in any one of claims 1 to 3, wherein the mixture is blown with air.
5. A process as claimed in any one of claims 1 to 4, wherein the cross-linkable polymer is a thermoplastic elastomer.
6. A process as claimed in claim 5, wherein the cross-linkable polymer is a block copolymer which comprises at least two terminal poly(monovinylaromatic hydrocarbon) blocks and at least one central poly(conjugated diene) block.
7. A process as claimed in claim 6, wherein the block copolymer is of formulae  $A(BA)_m$  or  $(AB)_nX$  wherein A represents a block of predominately poly(monovinylaromatic hydrocarbon) and wherein B represents a block of predominately poly(conjugated diene), wherein x represents the residue of a multivalent coupling agent and wherein n is an integer  $\geq 1$  and m is an integer  $\geq 1$ .

8. A process as claimed in any one of claims 1 to 7, wherein the amount of cross-linkable polymer in the mixture of bitumen and cross-linkable polymer is at least 3% wt, based on total amount of bitumen and cross-linkable polymer.
9. A polymer-modified bitumen composition obtainable by a process as claimed in any one of claims 1 to 8.
10. Use of a polymer-modified bitumen composition as claimed in claim 9 in paving applications.



Application No: GB 0227118.7  
Claims searched: 1-9

Examiner: Jason Scott  
Date of search: 16 May 2003

## Patents Act 1977 : Search Report under Section 17

### Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance	
X, Y	X: 1-5 & 8-10 Y: 6 & 7	GB 1325847 A	BRITISH PETROLEUM CO See whole document and in particular page 2, lines 40-59 & the examples.
X, Y	X: 1-5 & 8-10 Y: 6 & 7	GB 1304238 A	BRITISH PETROLEUM CO See whole document and in particular page 1, lines 28-46 & the examples
X, Y	X: 1-5 & 8-10 Y: 6 & 7	GB 886885 A	HUSKY OIL COMPANY See whole document and in particular page 2, lines 43-49 & page 116-122.
X	1-4, 9 & 10	GB 717050 A	COAL TAR RES ASS See whole document and in particular page 1, lines 50-64 and example II.
Y	6 & 7	DE 19726620 A	PARAFFINWERK WEBAU GMBH See whole document and in particular
X	1-4, 9 & 10	WPI Abstract Accession No 1991-365153 & JP 3244690 A COSMO (31.10.91) See abstract	

### Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

### Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC<sup>v</sup>:

C3K; C3L; C3M; C3N

Worldwide search of patent documents classified in the following areas of the IPC<sup>v</sup>:

C08J; C08K; C08L

The following online and other databases have been used in the preparation of this search report:

ONLINE: WPI, JAPIO, EPODOC